Analysis of Performance Degradation of Silica Gels after Extended Use Onboard the ISS

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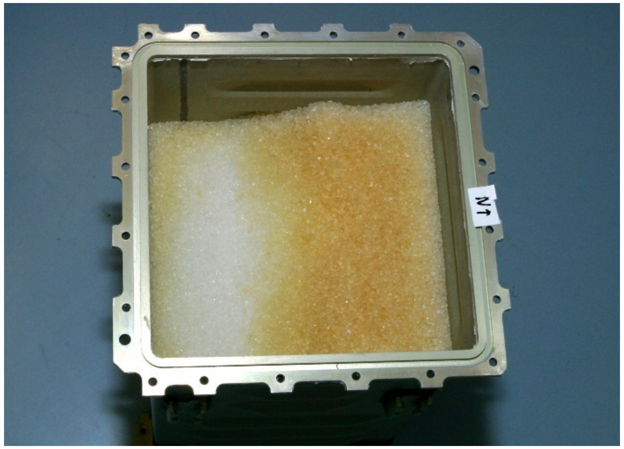
Gregory E Cmarik – Jacobs Space Exploration Group

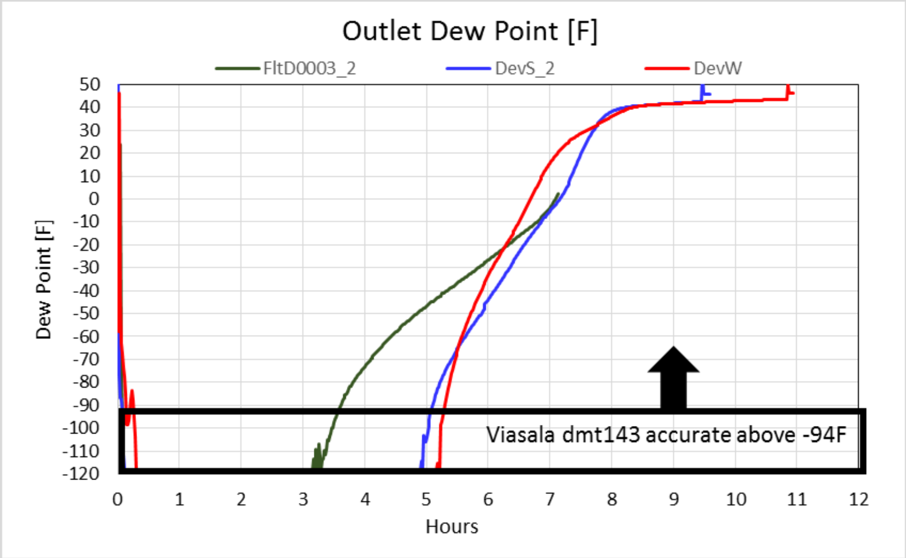
James C Knox – Jacobs Space Exploration Group

Timothy L Huff – NASA/MSFC/EM22

Background

- Closed-loop life support is an ultimate goal in ECLSS
- Long-term reliability is a need
- For CO_2 removal and downstream reduction, water vapor is a major challenge
- Desiccant beds have shown reduced performance after extended use
    - An orange discoloration coincidental to performance loss





A Brief History of Tests

- Chemical contamination (siloxanes, etc.) was identified and correlated with performance loss
    - CDRA-3 materials showed substantial quantities
- Capacity <u>loss</u> increases nearer to system inlet
    - Silica gel capacity loss of more than half at the inlet
    - Zeolite 13X in desiccant bed (inlet layer and residual layer) was unaffected
- New samples arrived from CDRA-4 bed disassembly
    - Similar discolorations observed

More Testing is Needed!

Chemical Contaminants

- Siloxanes D3-D6 are a major focus
- CDRA-3 samples nearest inlet show elevated levels of siloxanes among other trace contaminants
    - Much higher amounts on desiccant bed d1 than d5
- CDRA-4 samples
    - Repeat test method
    - Most samples show no detectable traces

No contaminants in new samples!

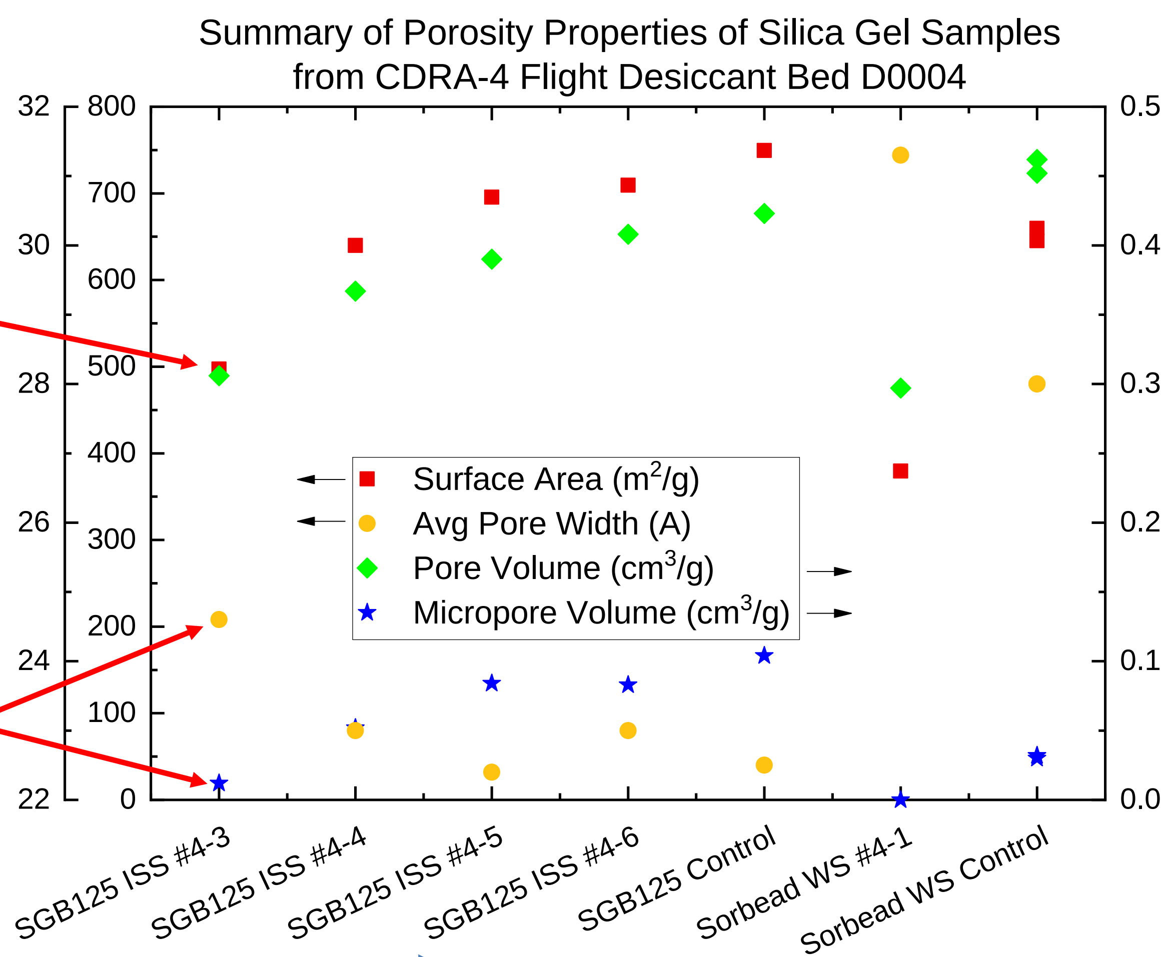
Table 1: Detectable siloxane concentrations on samples from CDRA-3 and CDRA-4 desiccant beds.

Sample ID	D3	D4	D5	D6
CDRA-3	[μg/g]	[μg/g]	[μg/g]	[μg/g]
1-5 sn D0001	232	73	280	162
1-8 sn D0001	-nd-	-nd-	-nd-	-nd-
5-7 sn D0005	6.6	5.7	8.7	9.9
5-9 sn D0005	-nd-	-nd-	-nd-	-nd-
Grade 40 Control	-nd-	-nd-	-nd-	-nd-
Dosed SG40 Sample (D5 @5mg/g)	-nd-	44	est. 2000-4000	75
CDRA-4	D3	D4	D5	D6
SGB-125 Control	-nd-	-nd-	-nd-	-nd-
Glass Bead	-nd-	-nd-	-nd-	-nd-
Sorbead WS #3-1	-nd-	-nd-	-nd-	-nd-
Sorbead WS #4-2	-nd-	12.13	6.58	13.98
SGB125 #3-3, 4, 5, 6	-nd-	-nd-	-nd-	-nd-
SGB125 #4-3, 4, 5, 6	-nd-	-nd-	-nd-	-nd-
13X #4-8, 9, 10	-nd-	-nd-	-nd-	-nd-
Control 1, 2	-nd-	-nd-	-nd-	-nd-
Spiked Sample	-nd-	40	10	10

Porosity

Loss of surface area
Loss of total pore volume

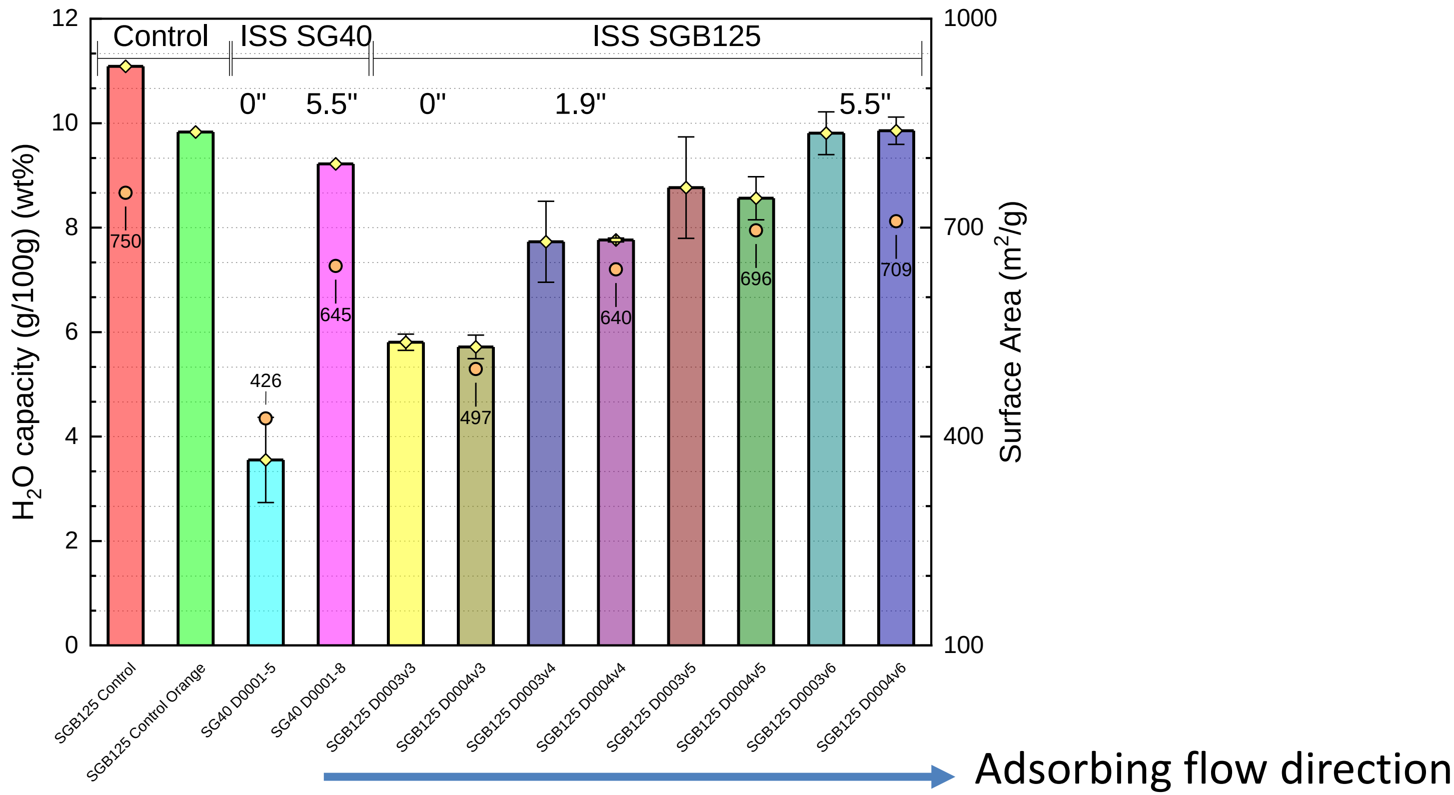
Increase in average pore radius
Loss of micropore volume



Adsorbing flow direction

Capacity

- Capacity and surface area correlate strongly
  - This is not a surprise, surface area is a cornerstone of adsorption



Search for Causes

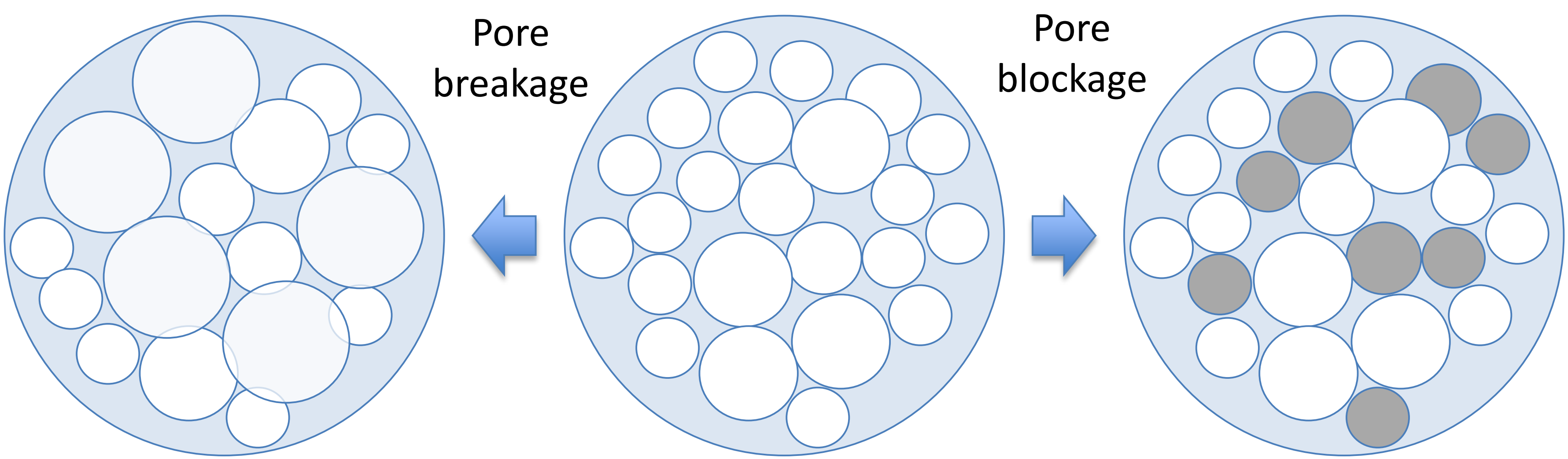
- Chemical alteration mechanisms
  - Contaminant reversible/irreversible adsorption
  - Deactivation of hydrophilic Si-OH groups
    - Due to chemical reaction
    - Due to thermal regeneration
- Physical alteration mechanisms
  - Pore closure
  - Pore wall breakage
- Until now, not enough data existed to study the possibilities
  - Tests on the ground were insufficient for replicating effects

Chemical Alteration

- Thermal deactivation mechanism is discounted
  - Requires in excess of 250°C to become a relevant mechanism
- Chemical deactivation mechanisms are considered unlikely
  - Irreversible adsorption mechanisms have not been identified
    - Dimethylsilanediol (DMSD) may be a cause but not a 100% match
  - Reversible adsorption (hydrophobic pore coatings) is unlikely due to lack of detection in extractions
- Orange discoloration attributed to traces of iron oxide
  - Iron (among many trace metals) is known to be present within the silica gel from initial manufacture
    - Oxygen is omnipresent in the pore spaces
  - Iron possibly introduced from upstream systems

Physical Alteration

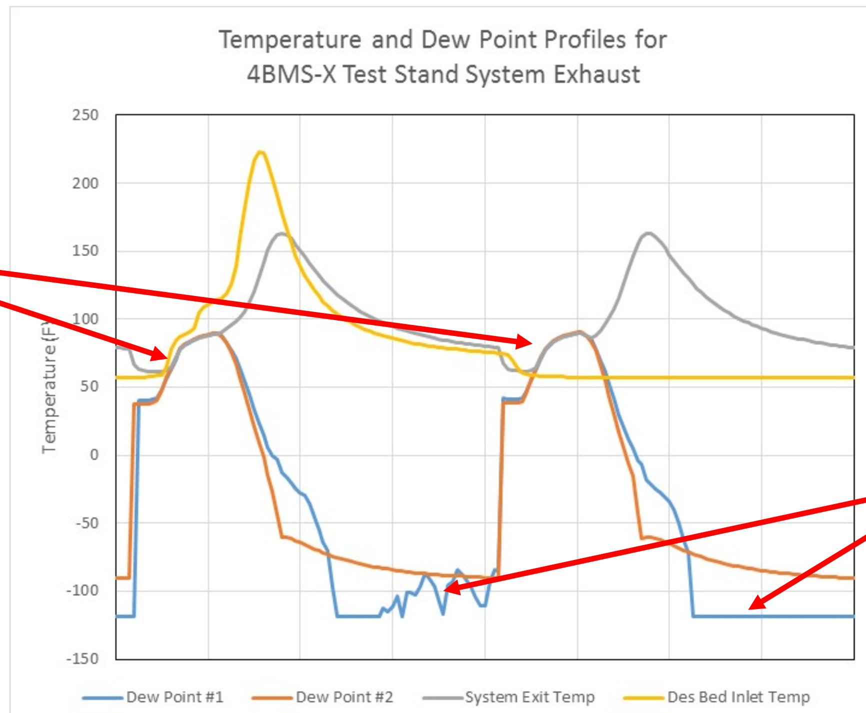
- Severe physical alteration of the interconnected porous network of the microporous silica gel is likely
  - The combination of measured porosity changes indicates the network of pores is altered



Proposed Mechanism

- Strongest correlation to the observed results:
    - Full-capacity adsorption (θ = 1) and desorption (θ = 0)
        - Θ is fractional loading

100%
Relative
Humidity



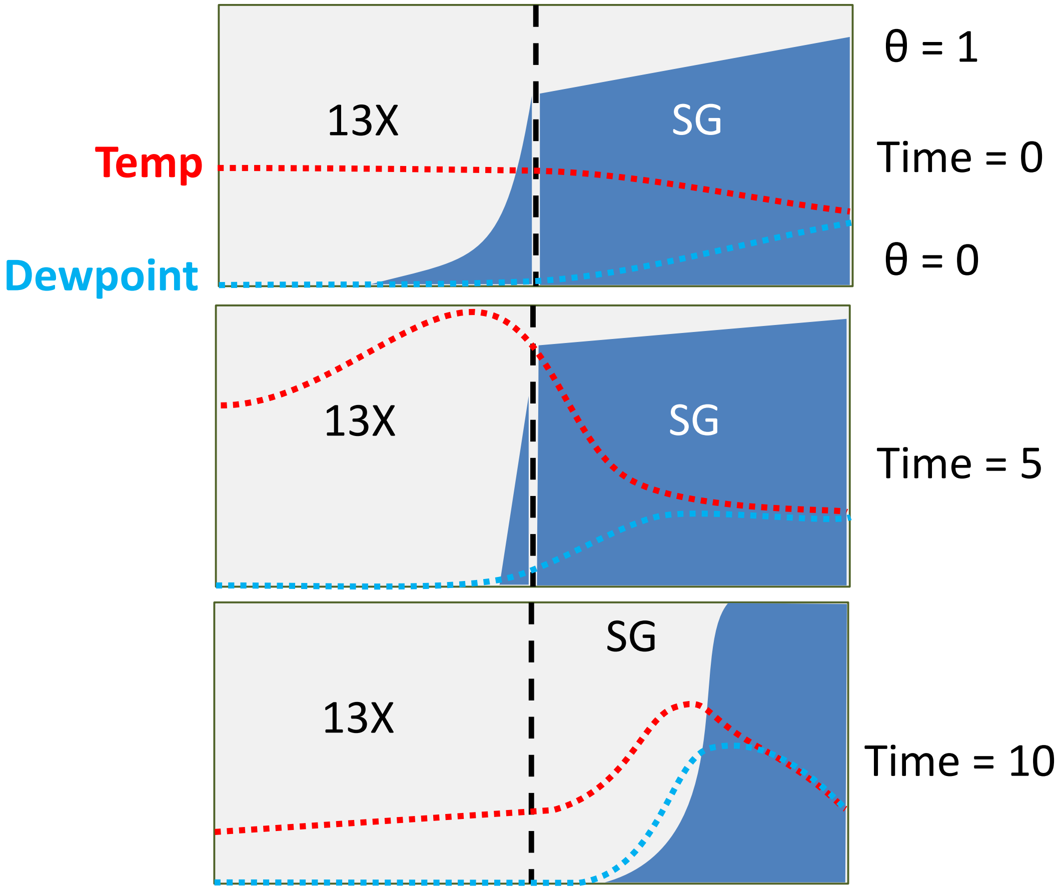
Completely
Dry

Proposed Mechanism

- Two waves propagate through bed
  1. Concentration
  2. Temperature

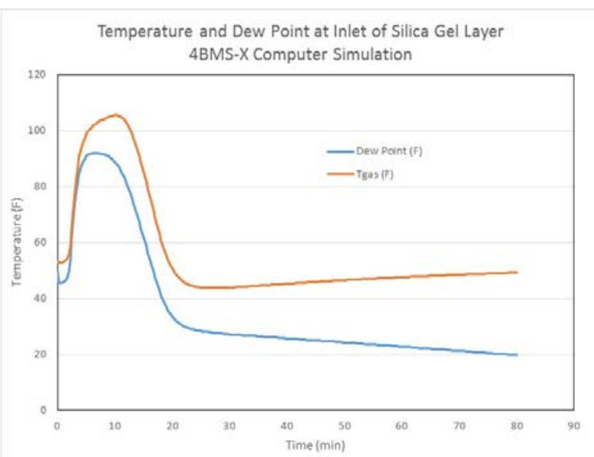
Desorb Flow

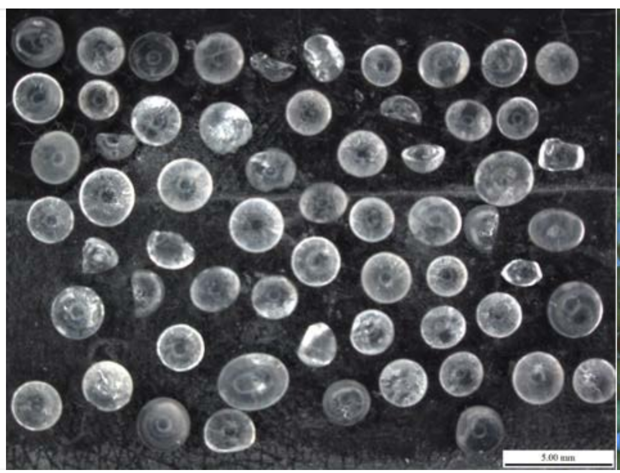
Loading
and
Relative Humidity

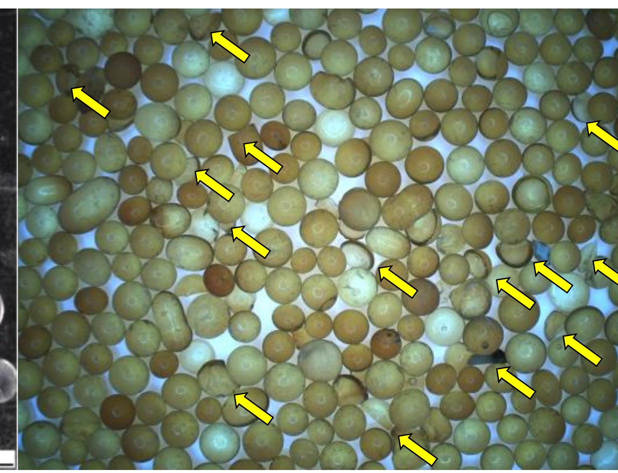


Additional Evidence

- Correlating facts
  - 100% RH – liquid water droplet formation – causes silica gel bead breakage
    - Broken beads found in sample vials – match misting test results
  - Simulation shows 100% RH condition occurring
  - Water is occasionally observed condensing at system outlet







Summary and Recommendations

- Search for cause of silica gel discoloration and degradation
  - Chemical analysis
  - Porosity analysis
- Proposed mechanism is that ‘full capacity sorption cycling’ causes physical degradation of pore system
  - Possibly unavoidable behavior of a 4-bed architecture
  - Major point to consider for next-gen 4-bed system
    - Sneak peek: new system does not show this behavior

Look forward to 4-Bed Systems

- Is this an inherent flaw?
    - No! The cause is bed size mismatch
    - Extra-large 5A-based sorbent beds in CDRA (and its ground-based equivalents) is likely cause
        - Excessively large heat wave transferred to desiccant bed causes the extreme concentration wave
    - Initial data from the development unit for next-gen 4-bed technology does not show the 100% RH condition
        - Smaller 13X-based sorbent bed does not cause the same overwhelming heat wave and thus large concentration wave

Acknowledgements

Additional contributors of data include C. Doug Wingard, Richard Boothe, Timothy Giesy, and Matthew Kayatin. The high level of detail included in the flight desiccant bed handling and breakthrough reports by Warren Peters and Chris Stanley were invaluable. Finally, thanks to Johnny Maroney for contributions to the final works.

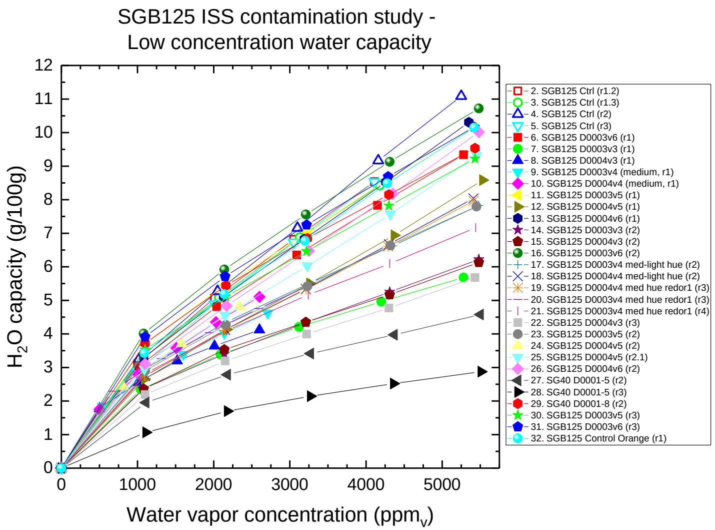
Questions?

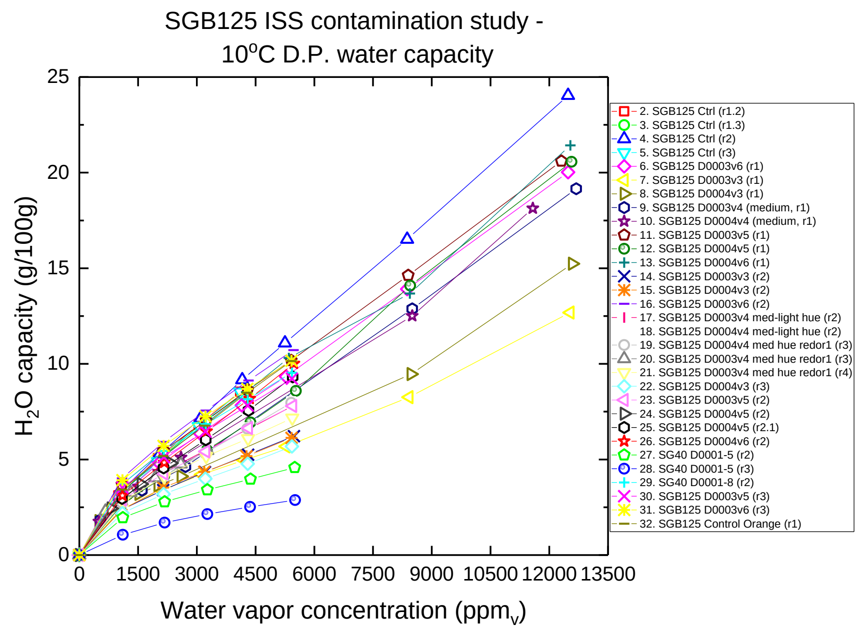
Backup Slides

Sample ID and info

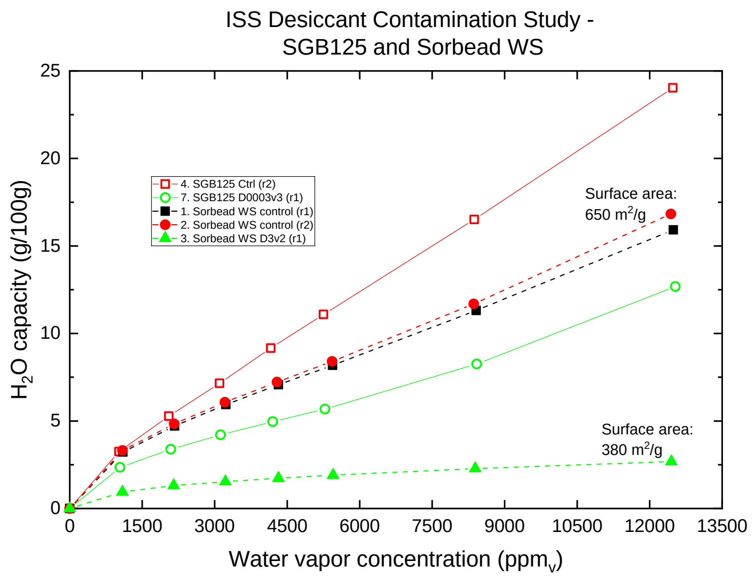
Sample ID	Material	Location	Condition
#3-1, 2	Sorbead WS	Guard layer, bed inlet	Strongly discolored Sorbead WS
#3-3	SGB125	Bulk Desiccant layer, 0” depth	Extremely discolored SGB125, some fractured beads
#3-4	SGB125	Bulk Desiccant layer, 1.9” depth	Strongly discolored SGB125
#3-5	SGB125	Bulk Desiccant layer, uncertain depth	Mostly clear SGB125, intermixed slight discolored beads
#3-6	SGB125	Bulk Desiccant layer, 5.5” depth	Mostly clear SGB125, intermixed slight discolored beads
#3-8, 9, 10	544 13X	Residual Desiccant Layer	Zeolite beads, Grade 544 13X, no discoloration
Sample ID	**Material**	**Location**	**Condition**
#4-2	Sorbead WS	Guard layer, bed inlet	Strongly discolored Sorbead WS
#4-3	SGB125	Bulk Desiccant layer, 0” depth	Extremely discolored SGB125, some fractured beads
#4-4	SGB125	Bulk Desiccant layer, uncertain depth	Strongly discolored SGB125
#4-5	SGB125	Bulk Desiccant layer, uncertain depth	Mostly clear SGB125, intermixed slight discolored beads
#4-6	SGB125	Bulk Desiccant layer, 5.5” depth	Mostly clear SGB125, intermixed slight discolored beads
#4-8, 9, 10	544 13X	Residual Desiccant Layer	Zeolite beads, Grade 544 13X, no discoloration

SGB isotherms





Sorbead WS isotherms



13X isotherms